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Spectrally resolved detection of NH_3 at ppb level

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Abstract. Photoacoustic detection of 30 ppb ammonia in air is demonstrated with a signal to noise ratio of 40, using a 400 MHz tunable CO_2 laser as radiation source. Interference from CO_2 is controlled by monitoring near the Doppler limit and by using phase information to separate the two signals. Wall adhesion is studied quantitatively. It is shown that the walls constitute a reservoir of fixed size, which is filled up at a rate proportional to the NH_3 concentration.

1 Introduction

Ambient air contains ammonia in concentrations which typically range from 0.1 ppb over sea water, to tens of ppb in regions of intensive livestock breeding. It has been known for a long time that photoacoustics, using a CO_2 laser as radiation source, will in principle provide the required sensitivity for monitoring these concentrations. However, two problems have blocked the way for practical use of this scheme. The first problem is associated with the presence of CO_2 in the atmosphere. The line strength of a strong NH_3 line is typically 5000 times larger than that of the CO_2 hot band transitions which will absorb at the center of each CO_2 laser line. Hence, an ambient CO_2 concentration of 400 ppm will be equivalent to an NH_3 concentration of about 80 ppb and thus lead to a sizeable interference problem. This can be dealt with by using isotopic CO_2 lasers [1], by using Stark modulation techniques [2], or by measuring in a number of different CO_2 lines [3] and combining the results. We here describe a different approach which is technically considerably simpler, while still providing the required discrimination.

The second problem is related to the strong tendency of NH_3 to stick to surfaces. The photoacoustic signal is generated in a cell, and it is very difficult to ensure that the concentration in the gas phase inside the cell is representative of the source. Furthermore, the equilibrium between the gas phase and the walls may be approached with excessively large time constants. In fact, the absence of equilibrium sometimes have lead to quite exaggerated claims concerning the sensitivity.

In this paper we present a solution to the CO_2 interference problem based on the use of a widely tunable CO_2 laser combined with exploitation of photoacoustic phase information. The method is subsequently used for performing quantitative studies of wall adhesion.

2 The photoacoustic setup

The radiation source is a small 400 MHz tunable CO_2 laser, electrically pulsed at 800 Hz, similar to that which has been previously used for detecting NH_3 at ppm concentrations in power plant emission [4]. It provides 400 mW at the center of the 9R30 line, and in the Doppler limit its tuning

range allows recording of the resolved rotation-vibration absorption profile of the $sR(5,0)$ ammonia transition at an offset of -190 MHz.

The photoacoustic cell is shown in Fig.1. It consists of a 20 cm long organ pipe of stainless steel, resonant at 800 Hz, and contained in a glass housing with spherical baffles and ZnSe Brewster windows. A Knowles microphone is mounted behind a hole at the center of the acoustic resonator. The signal was preamplified, and the amplitude and phase were measured with a dual phase lock in amplifier.

Fig.1 Resonant photoacoustic cell.

Fig.2 Flow system for generating low concentrations by dynamic mixing.

3 Gas handling system

Controlled concentrations of NH_3 in N_2 or in air were established by dynamic mixing, using a system of calibrated mass flow controllers shown in Fig.2. A certified mixture of 42 ppm of NH_3 in N_2 , provided by UCAR, was supplied to either of two controllers with a maximum flow rate of 10 and 100 ml/min STP, and a resolution of 1%. This gas was diluted by either N_2 or air supplied from a controller of flow rate 500 ml/min STP. The flows were combined, and allowed to flow freely into the atmosphere. Gas to the cell was sampled at a rate between 50 and 250 ml/min STP through a needle valve from a tee inserted in the combined flow. In this way the NH_3 concentration could be changed without affecting the pressure in, or the flow through the cell.

Since the photoacoustic responsivity as well as the wall effects are influenced by the presence of water [3, 5], provision was made for humidifying the buffer gas by letting it bubble through water after leaving the flow controller. The pressure was measured at the center of the cell with an absolute pressure meter of 0.1 mBar resolution, calibrated against a mercury manometer.

Using this system, and allowing the necessary time for equilibrium with the walls of the cell, reproducible and reliable measurements could be made. It should be strongly emphasized that when attempting to generate low concentrations by stepwise dilution in containers, wall effects imply a high risk of arriving at concentrations quite far from those aimed for.

4 Calibration

All flow controllers were calibrated using a water displacement flow meter. Requiring the flow rate to be at least 10 times the resolution limit, the lowest concentration that could be generated was 84 ppb. Calibration of the photoacoustic responsivity was performed at 27.5 mBar and room temperature with moist N_2 as buffer gas over the range 84 to 7000 ppb, with results as shown in Fig.3. Within the experimental scatter of the data points, the response is linear in concentration over this range, as expected. The measured sensitivity of $0.17 \mu V$ per ppb, combined with an rms noise limit of

0.14 μV , leads to a minimum detectable concentration of 0.8 ppb at a signal to noise ratio of 1. Increasing the pressure to 150 mBar will increase the photoacoustic response by a factor of 4, and hence improve the sensitivity significantly. However, the associated line broadening will aggravate the problems associated with CO_2 interference, and 27.5 mBar was found to provide a convenient compromise between sensitivity and selectivity.

Fig.3 Photoacoustic response as a function of NH_3 concentration with wet N_2 as buffer gas.

Fig.4 Photoacoustic amplitude and phase as a function of frequency tuning.

5 Selectivity

Recordings of photoacoustic amplitude and phase are shown in Fig. 4 for about 30 ppb NH_3 in moist air. At the center of the tuning range, the signal is completely dominated by CO_2 , present in the air at a concentration of about 400 ppm. The amplitude is 14.5 μV , equivalent to 85 ppb of NH_3 , and the phase is at 196° . Owing to kinetic cooling [4, 3] the CO_2 signal is 0.6 ms delayed relative to the NH_3 signal, corresponding to a phase lag of 170° . Thus, as the laser frequency is scanned towards negative offset, the phase of the combined signal will experience a sudden change, being eventually completely controlled by NH_3 . At the offset where the combined phase changes most rapidly, the combined amplitude becomes almost zero, reflecting the nearly complete destructive interference between the photoacoustic signal generated by CO_2 , and that generated by NH_3 . It is precisely this feature that greatly facilitates the discrimination between the two signals, and thus provides the selectivity.

6 Wall absorption

The tendency of NH_3 to stick to surfaces is known to be the major problem in instrumentation for dynamic monitoring of NH_3 . Some semi quantitative experiments have been performed, using a leaf chamber technique [6]. We have studied the problem by applying a step change in the input concentration to the cell, starting from zero concentration. Initially, the NH_3 molecules will settle on the wall in the vicinity of the entrance, and few of them will survive to the acoustic resonator and be detected. As the wall gradually becomes saturated, the photoacoustic response will increase, and eventually reach a steady level. If the response is plotted as a function of time, the area in the graph between the asymptote and the actual response curve is a measure of the number of molecules lost to that part of the wall which is located between the gas entrance and the detection region.

Measurements have been carried out at concentrations of 423 ppb and 4516 ppb, in both cases with wet N_2 as buffer gas. The cell was prepared by flushing with moist N_2 for several hours. From the measured flow rate and the known responsivity it is straightforward to evaluate the number of molecules lost to the wall in the two cases. At the lowest concentration, saturation was not reached during the 6 hours duration of the experiment. In this case, the photoacoustic signal is assumed to approach the asymptote exponentially, with a time constant of 3 hours, as determined by the slope of the data for times larger than 180 minutes.

Using this method, the loss to the wall was found to be 0.45 and $0.39 \mu\text{Mol}$ respectively, both with an estimated uncertainty of about 20%. Considering the factor of 10 difference between the input concentrations, we may conclude that the wall constitutes a reservoir of fixed size, and that it is filled up at a rate which is essentially proportional to the concentration of NH_3 in the gas phase.

With a total surface area of about 360 cm^2 , we find that each NH_3 molecule occupies an area of $3.2 \times 3.2 \text{ \AA}^2$. This suggests that a monolayer is formed on the wall, and that the existence of this layer effectively prevents further deposition.

7 Conclusion

It is possible to measure NH_3 at sub ppb levels in air, using a normal isotope CO_2 laser with enough tunability to allow recording of Doppler limited absorption profiles. Discrimination against absorption from CO_2 in the air is provided by photoacoustic phase information. The walls of the cell constitute a reservoir of fixed size for NH_3 molecules. It is filled up at a rate proportional to the gas phase concentration, and this leads to very long time constants at low concentrations.

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Fig.5 Photoacoustic response as a function of time for a step function in input concentration applied at $t=0$.